

ANTONIA LABORATORY OPPAU

BAG # 2168 4/30/03

T.O.M. Microfilm Reel #1
December 30, 1941CONVERSION OF A SYNTHETIC OLEFIN (Dr. Kotschmar)
INTO OXO-ALCOHOLS

The olefin mixture from the carbon monoxide-hydrogen synthesis (exp. D 259, b.p. 195-320°C.) supplied by Dr. Kotschmar was analyzed as such and in its fractions.

Analysis of the Olefin Mixture

Iodine number: 98

Hydrogenation iodine number (PtO₂): 95

C 81.86; H 13.66; C + H 95.52; H active 0.15; OH number (Verley, Bolsing) 55;

OH number (from act. H) 58; acid number 25.7; sap. number 30.4; ester number 4.7;

CO number 32. The olefin mixture was fractionated into fractions under 5 mm in a column with 7 theoretical plates. (See table 1)

From the analytical data of the individual fractions it will be seen that the product is a 10-20 C-atom olefin mixture contaminated with alcohol and acid constituent and whose average olefin content lies between 60 and 70%. As will be seen from Table 2 and, chiefly, 4, the lower fraction must contain constituents with about 8 C-atoms. In addition there are alcohols in amounts of between 20-25% and acids between 5 and 8%. However, this only holds as long as molecules with several functions are not partially present.

If the olefin mixture is subjected to the conditions of the oxo-reaction and the product is hydrogenated to alcohol, 210.5 g of conversion products are obtained as an average of several experiments from 200 g olefin mixture. Taking an iodine number of 98 as basis, this yield would be about 53.7% of the theoretical yield. The crude oxo-alcohol mixture furnished the following analytical data:

C 78.77; H 13.73; OH number 190; CO number 5; Acid number 4.4; sap. number 24; O 7.50; cobalt 0.037%.

This mixture was also fractionated under 5 mm pressure in a column with 7 theoretical plates. (See table 2).

From the tabulation it will be seen that the alcohol contents of the individual fractions increase with increasing boiling point from 47 to as high as 90%, showing that the non-alcoholic constituents are enriched in the first fraction because of their lower boiling points. On the basis of the OH number and the mol. wt. determination the distillate (85%) contains alcohols with 9 to 18.4 C-atoms. The alcohol content of the total mixture has increased from about 22% to about 61%.

Since a separation of the hydrocarbon constituents from the alcoholic constituents is impossible by distillation alone, as will be seen plainly from Table 2, the boric acid ester method was used for separating the pure alcohol constituents (cf. Ger. pat. 444,640). For this purpose the alcohols of the hydrocarbon-alcohol mixture are converted with boric acid or boric acid triacetate into their high-boiling boric acid esters, whereupon the hydrocarbon-constituents are distilled off under reduced pressure and the alcohols are liberated from the residual boric acid esters by saponification.

The oxo-alcohol mixture, however, contained even in the very initial material small amounts of free acids and esters (cf. Tables 1 and 2) which were separated by saponification before using the boric acid ester method. Through this saponification the oxo-alcohol mixture was divided into about 90% of unsaponifiable matter and about 4.5% of free acid.

Unsaponifiable: acid number 0; sap. number 0; OH number 210; CO number 3.

Acid " " 390; " " 390; " " 20; " " 3.

~~The figures for the unsaponifiable matter show that the OH number has increased~~ from 190 to 210 by separation of saponifiable constituents and that the mixture is now practically one consisting of alcohols and hydrocarbons (CO number 3).

In the attempt of separating this alcohol-hydrocarbon mixture directly by the boric acid ester method into a hydrocarbon and an alcohol fraction it was found that on distilling off the entire hydrocarbon fraction, boric acid esters of lower alcohols also came over, thus preventing a truly quantitative separation.

In a model test with n-hexylalcohol it was found that the neutral boric acid ester of this alcohol boils at 135-138°C at 1.5 mm.

It was therefore necessary to divide the unseparable matter of the oxo-alcohol mixture into 30° fractions and to subject these fractions separately by the boric acid ester method.

As may be expected from Table 2, it will be seen from Table 3 that the largest increases in the OH number occur in the lower fractions when applying the boric acid ester method while the higher fractions practically consist of pure alcohol.

The oxo-alcohols fractionally separated from the hydrocarbon constituents in the form of boric acid esters were united and subjected to close-cut fractionation in a column with 16 theoretical plates. The intention was to find whether there are any distillation steps which eventually may result in the separation of homogeneous alcohols of definite structure (See table 4).

This, however, is not the case; the distillation curve exhibits no steps.

From the tabulation in table 4 it will be seen that the alcohols are between C₇ and C₁₇. The agreement of analytical data (mol. wt., OH number, C, H, O) satisfies C₇ to C₁₄ compounds, and for the higher fractions an excess of oxygen is found above the calculated values. The low and fluctuating melting points of the increasing fraction are particularly striking. This shows the presence of predominantly branched alcohols. This discovery agrees with the findings of Dr. Leithe who claims that synthetic olefins are branched to the extent of about 30% through the addition of the formyl radical in α and β -position to the double bond. The oxo reaction

induces additional branching, regardless of the position of these radicals, so that normal oxo-alcohols can not be expected in large quantities from synthetic olefins of this type.

sgd. Nienburg
sgd. Keunecke

This investigation was carried out in the group of Dr. Keunecke together with other work during the period of March to July, 1941.

Translation: GRL:ej
Richmond: 2-8-46

mb